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Ecofriendly synthesis of biscoumarin derivatives catalyzed by EDTA-modified magnetic animal bone meal nanoparticles in water

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ABSTRACT

In this research, magnetic animal bone meal nanoparticles functionalized with ethylenediaminetetraacetic acid (Fe_3O_4@ABM-EDTA) is reported as a green recyclable catalyst that catalyzed synthesis of biscoumarin derivatives in water. The catalyst was characterized by the Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), differential thermogravimetric (DTG), scanning electron microscope (SEM) and X-ray diffraction (XRD). This study has demonstrated that Fe_3O_4@ABM-EDTA can act as an efficient catalyst for synthesis of biscoumarines in the presence of water as solvent at reflux conditions. A wide range of aldehydes could react with 2-hydroxycoumarin and give biscoumarin derivatives in excellent yields. Moreover, Fe_3O_4@ABM-EDTA was magnetically recovered and reused for five cycles without any significant loss of efficiency.

Keywords: *Green catalyst, Biscoumarin, Animal bone meal, Ethylenediaminetetraacetic acid, Magnetic nanoparticles.*

1. Introduction

Green chemistry is the design and development of chemical products and processes to reduce or eliminate the use and generation of hazardous substances [1]. Development of environmentally benign synthetic methods have recently attracted the attention of organic chemists. In the context of green chemistry, the solvent and catalyst play a crucial role. Catalysts accelerate chemical reactions, increase yields and reduce waste product formation. Therefore, in recent years, the use of non-toxic and reusable catalysts has been developed. Natural catalysts, bio-base catalysts, solid supported catalysts are examples of this category [2]. Among them, solid supported catalysts have attracted much attention, because they have many advantages, such as ease of catalyst separation and high catalytic activity. Nanoparticles especially core-shell magnetic nanoparticles have been used as support for homogenous catalysts [3]. These magnetic catalytic systems have high surface area and it can be separated from product solution by an external magnet, this can prevent the loss of solid catalyst that occurs in conventional separation methods [4, 5].

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Hydroxyapatite (HAP) is a main part of animal bones [6]. The ABM is a natural and inexpensive solid support which can contribute to the development of catalytic processes and reduce environmental problems.

Ethylenediaminetetraacetic acid (EDTA) is a well known chelating agent [7]. Its immobilization on the different supporting materials such as silica gel [8], chitosan [9], polystyrene [10] and cellulose [11] have received much attention for the metal adsorption purposes. In addition, the use of EDTA-Pd as a heterogeneous catalyst for the Suzuki–Miyaura reactions and EDTA-Pt for the hydrosilylation of olefins has been reported in the literature [12, 13]. EDTA is used as a ligand that is attached to Pd and Pt center to stabilize the catalyst.

While homogeneous and heterogeneous protic acids and Lewis acids are used in catalyzed organic reactions, most of these catalysts suffer from some disadvantages such as use of expensive and corrosive reagents, toxic transition metals, sensitivity to moisture and non availability [14]. It seems that EDTA could be an environmental benign catalyst alternative for some hazardous catalysts. EDTA is soluble in water and some organic solvents and acts as a homogeneous catalyst. Heterogenization of EDTA by immobilizing on a solid support could solve this problem.

Biscoumarin and its derivatives are significant due to their biological activities such as urease inhibitors [15], HIV inhibitory activity [16], anticoagulant activity [17], treatment of thrombosis [18], Recently, a number of methods have been reported for the synthesis of biscoumarins by reaction of 4-hydroxycoumarin and various aldehydes [19-28]. The importance of developing new environmentally benign methods led us to consider EDTA as a nontoxic acidic compound and ABM as an inexpensive and available support for preparation of a green heterogeneous organocatalyst.

To the best of our knowledge, there is no report on the use of EDTA as a Bronsted acid catalyst in the organic synthesis. Herein, we report the preparation of EDTA incorporated on a surface of ABM magnetite nanoparticles, which catalyzed the synthesis biscoumarins in water as a solvent (Scheme 1). The magnetic catalyst could be easily isolated from the reaction mixture by an external magnet and reused several times without a significant reduce in activity.

2. Experimental

2.1. General

All chemicals, including $FeCl_3 \cdot 6H_2O$, (3-aminopropyl) triethoxysilane (APTES), aldehyde derivatives and 4-hydroxycumarine were purchased with high purity from Fluka and Merck (Darmstadt, Germany). Ethylenediaminetetraacetic acid (EDTA) was purchased from Merck. ^{1}H NMR spectra were recorded with a Bruker Ultrashield 400 spectrometer. FT-IR spectra were obtained with potassium bromide pellets in the range 400–4000 cm^{-1} with a JASCO 6300 spectrometer. The morphology of the catalyst was studied by the scanning electron microscopy (HITACHI S-4160). Thermogravimetric analysis (TGA/DTA) was carried out under air atmosphere with a Mettler TA- 4000 thermogravimetric analyzer. Powder X-ray diffraction patterns was recorded on a Bruker, D8 ADVANCE with Co Kα (α =1.5406 Å) a voltage of 40 kV, and a current of 40 mA.

2.2. Preparation of magnetic Fe_3O_4 nanoparticles (Fe_3O_4-MNPs)

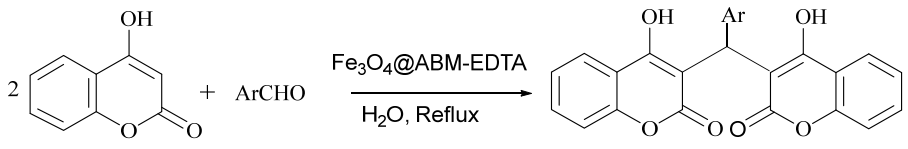
Magnetite nanoparticles (Fe_3O_4-MNPs) were synthesized according to the reported procedure [29]. $FeCl_3.6H_2O$ (2.35 g, 8.7 mmol) and $FeCl_2.4H_2O$ (0.86 g, 4.3 mmol) were dissolved in 40 mL deionized water. The resultant solution was stirred for 30 min at 80 ℃. Then 5 mL of NH_4OH solution was added with vigorous stirring to produce a black solid and the resultant mixture was stirred for another 30 min and then cooled to room temperature. The black magnetic nanoparticles were isolated by the magnetic decantation, washed several times with deionized water and then dried in an oven at 80 ℃

2.3. Preparation of ABM and surface modification of Fe_3O_4 -NPs with ABM

Animal bone meal was prepared according to the reported procedure [6]. The magnetite particles obtained in the previous step were covered with a layer of ABM. To this purpose, a suspension of ABM and magnetite nanoparticles (1:1 w/w) in ethanol was prepared. The mixture was ultrasonicated for 20 min. After ultra-sonication, the mixture was stirred for 12 hours at reflux conditions under Ar atmosphere. Then, the mixture was cooled to room temperature and ABM-coated magnetic nanoparticles were separated by an external magnet, washed with ethanol, and dried at 80 ℃.

2.4. Synthesis of Fe_3O_4@ABM-EDTA

EDTA anhydride synthesized according to the reported procedure [30]. EDTA (10.0 g, 34 mmol), was suspended in 16 ml pyridine. Then, 14 mL acetic anhydride was added to the solution and the mixture was stirred at 65 ℃ for 24 h. The solid product was filtered and washed with acetic anhydride and dry diethyl ether several times and dried in vacuum for 24 h. After this, Fe_3O_4@ABM (2 g) was added to the solution of 3-(aminopropyl) triethoxysilane (2 mL) in ethanol (50 mL) and the resultant mixture was refluxed under Ar atmosphere for 12 h. The amino-functionalized Fe_3O_4@ABM particles were separated by a magnet and were washed with ethanol and dried at 80 ℃ for 8 h. Finally, the prepared Fe_3O_4@ABM-NH_2 (5 g) and EDTA anhydride (10 g) were dispersed in ethanol/acetic acid solution (50 %, 50 mL) with vigorous stirring. The mixture was refluxed for 12 h. The resulted solid (Fe_3O_4@ABM-EDTA) was separated by an external magnet and was washed with acetone/water and dried under vacuum at room temperature [31]. The content of acid sites of the Fe_3O_4@ABM-EDTA was determined to be 1.1 mmol H^+ g^{-1} using acid-base titration.



Scheme 1. Synthesis of biscoumarin derivatives using Fe_3O_4@ABM-EDTA as catalyst.

2.5. General procedure for the synthesis of biscoumarin derivatives

A mixture of 4-hydroxycoumarin (2.0 mmol), aldehyde (1.0 mmol) and Fe_3O_4@ABM-EDTA (0.008 g) as the catalyst in water (5 mL) was heated under reflux conditions for the appropriate time. After completion of the reaction, (monitored by TLC), the catalyst was separated by an external magnet. The reaction mixture was allowed to be cooled to room temperature. The solid was filtered and recrystallized from ethanol.

3. Results and Discussion.

3.1. Characterization of catalyst

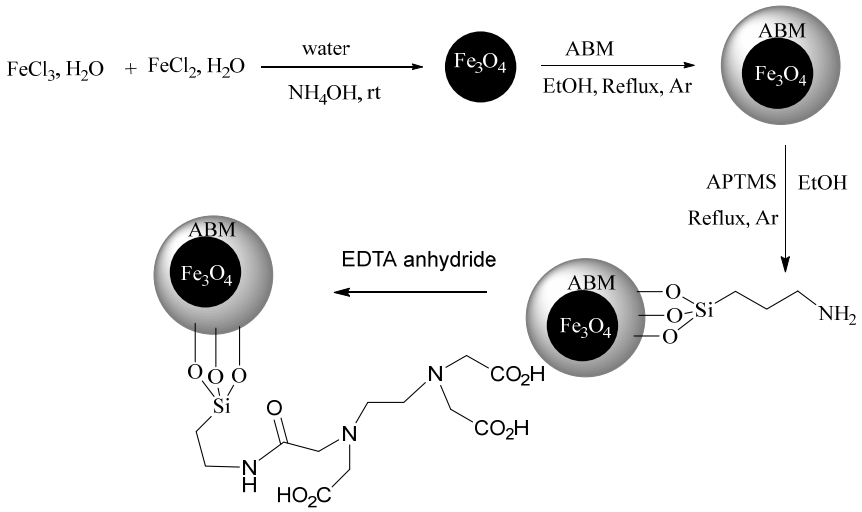
Fe_3O_4 magnetic nanoparticles (MNPs) were prepared by chemical co-precipitation from $Fe^{2+}$and Fe^{3+}in ammonia solution. The chemical stability of magnetic nanoparticles was improved by coating their surface with animal bone meal. Then, amino-coated Fe_3O_4 nanoparticles were obtained by coordination of bond formation between the 3-(aminopropyl)triethoxysilane and the ABM surface. Subsequently, Fe_3O_4@ABM-EDTA was prepared by the amidation reaction of amino groups with anhydride groups of EDTA anhydride (Scheme 2). The prepared catalyst was characterized by FT-IR, TGA and SEM. The bone meal obtained were characterized by X-ray diffraction (Fig. 1).

XRD pattern of the ABM showed the structure of the prepared sample was similar to the hydroxyapatite standard. Elemental analysis of ABM revealed the presence of phosphate (57.5%), calcium (38.4%), magnesium (3.33%), carbon (0.16%), hydrogen (0.13%), and nitrogen (0.48%).

The FT-IR spectra of the animal bone meal, Fe_3O_4@ABM and Fe_3O_4@ABM-EDTA were shown in Fig. 2. Fig. 2a showed the characteristic absorption peaks of sample ABM. The bond at 3571 cm^{-1} was attributed to the stretching vibration of the lattice OH^- and the medium sharp peak at 633 cm^{-1} was assigned to the OH deformation mode. The characteristic bonds for PO_4^{3-} appear at 570, 603, 962, 1049 and 1091 cm^{-1} [32]. Stretching mode of Fe–O appears at 570 cm^{-1} (Fig. 2b,c). In the spectrum of Fe_3O_4@ABM-EDTA, the characteristic absorption bands at 1409, 1695 and 3419 cm^{-1} confirm the successful bonded EDTA on the magnetite nanoparticles surface (Fig. 2c) [33, 34].

The morphology and size distribution of Fe_3O_4@ABM, Fe_3O_4@ABM-NH_2 and Fe_3O_4@ABM-EDTA were examined by SEM (Fig. 3). Scanning electron microscopy (SEM) revealed that Fe_3O_4@ABM particles have a nearly spherical shape (Fig. 3a). Fig. 3b shows that Fe_3O_4@ABM-NH_2 particles have similar morphological properties compared with Fe_3O_4@ABM except for the larger particle size. Fe_3O_4@ABM-EDTA exhibits smooth surface morphology as shown in Fig. 3c.

The thermal stability of Fe_3O_4@ABM-EDTA was determined by the TGA/DTA analysis (Fig. 4). The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) curve for Fe_3O_4@ABM-EDTA show a weight loss of about 1.7% at 72 ℃, due to the removal of volatile organic solvents. The decomposition of the organic groups supported on the magnetic animal bone meal occurs at temperatures of 215-532 ℃ and the amount of organic component was about 39% of the total solid catalyst.



Scheme 2. Preparation of Fe_3O_4@ABM-EDTA.

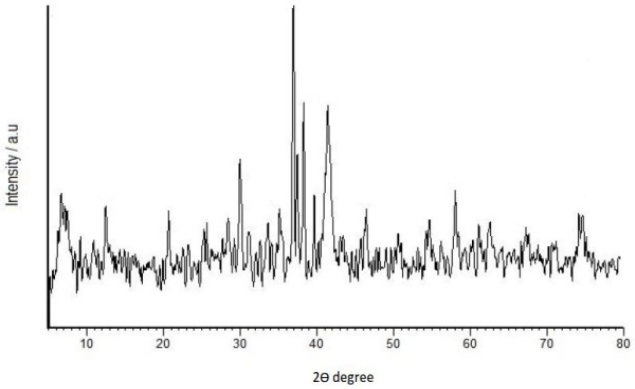


Fig. 1. XRD of ABM.

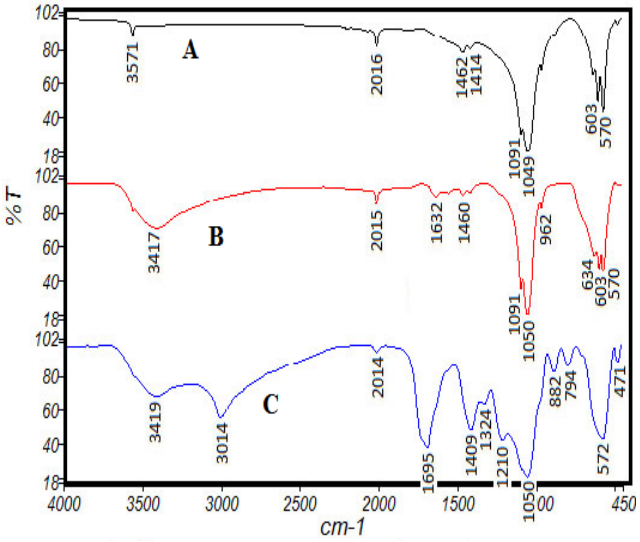


Fig. 2. FT-IR spectra of (a) ABM, (b) Fe3O4@ABM and (c) Fe3O4@ABM-EDTA.

3.2. Catalytic activity

The catalytic activity of the synthesized Fe_3O_4@ABM-EDTA was investigated in the synthesis of biscoumarins. Initially, the condensation reaction of 4-nitrobenzaldehydes with 4-hydroxycoumarin in the presence of a catalytic amount of Fe_3O_4@ABM-EDTA under solvent-free conditions was chosen as a model reaction. Interestingly, the corresponding biscoumarin was obtained in good yield. In order to optimize the reaction conditions for the synthesis of biscoumarins, the effects of solvent, temperature and the amount of catalyst were investigated. The model reaction was carried out in the various solvents and solvent-less conditions (Table 1, entries 1-7). The results showed that carrying out the reaction in H_2O gave the highest yield for the desired product (Table 1, entry 6). The effect of temperature was studied by carrying out the model reaction at different temperatures in ethanol (room temperature, 30, 50 °C and reflux conditions) and the best result was obtained at reflux conditions (Table 1, entries 11-14). At room temperature, the reaction did not take place and no formation of the respective products was detected after 1 h, (Table 1, entry 11). Afterwards, the influences of the catalyst amount on this reaction was investigated. The reaction was performed with 0.005-0.02 g of Fe_3O_4@ABM-EDTA as the catalyst. It was observed that the best amount of Fe_3O_4@ABM-EDTA is 0.008 g which afforded the desired product in 98 % yields (Table 1, entry 6). Increasing amounts of catalyst did not improve the yield or reaction rate (Table 1, entries 9 and 10). Based on above observations, a wide variety of aromatic aldehydes, containing both electron-withdrawing and electron-donating groups (Table 2, entries 1–10), 2-furylcarbaldehyde as heteroaromatic aldehyde (Table 2, entry 11), and aliphatic aldehydes derivative, such as cinnamaldehyde (Table 2, entry 12) were treated with 4-hydroxycoumarin to give the corresponding biscoumarin products. As shown in Table 2, a wide range of aldehydes could react with 2-hydroxycoumarin and give biscoumarin derivatives in excellent yields.

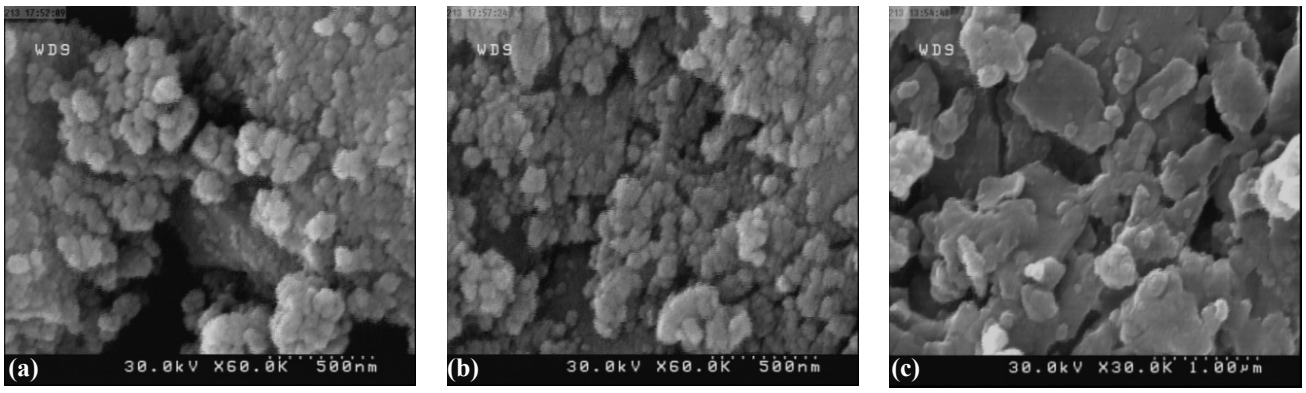


Fig. 3. The SEM image of (a) Fe_3O_4@ABM (b) Fe_3O_4@ABM-NH_2 and (c) Fe_3O_4@ABM-EDTA.

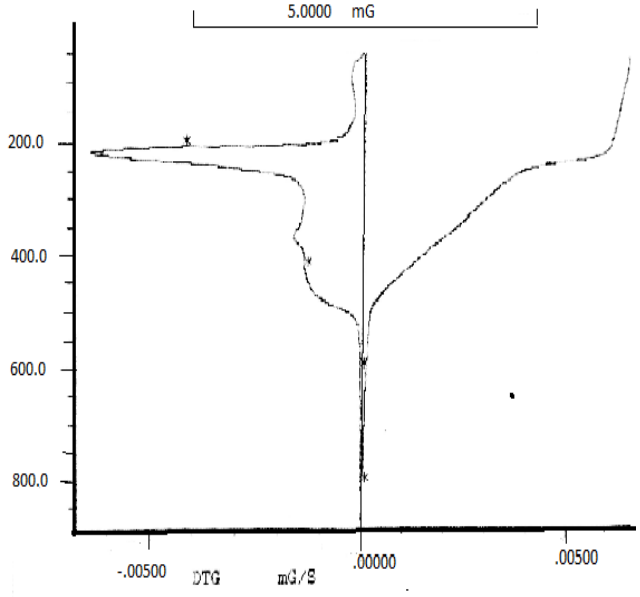


Fig. 4. TGA/DTG curves of Fe_3O_4@ABM-EDTA.

Reusability of the catalyst was studied through a condensation reaction of 4-nitrobenzaldehyde with 4-hydroxycoumarin under optimized conditions. In this procedure, after completion of the reaction, hot ethanol was added and the catalyst was easily separated from the product by an external magnet. The remaining catalyst was washed with ethanol to remove the residual product and dried in oven at 80 ˚C. The recovered catalyst was then added to fresh substrates under the same experimental conditions for five runs without a noticeable decrease in the product yield and its catalytic activity (The yields were 98, 98, 95, 90 and 85%, respectively).

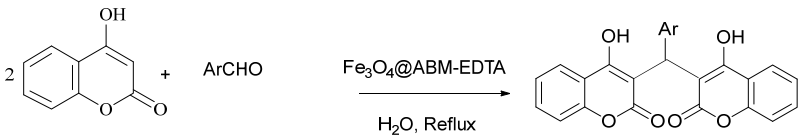
To show the merit of the present work in comparison with previously reported results in the literature, we summarized some of results for the synthesis of biscoumarin derivatives in Table 3. As shown in Table 3, Fe_3O_4@ABM-EDTA can act as effective catalyst with respect to reaction times and yields.

Table 1. Optimization of reaction conditions for the synthesis of biscoumarin.[a]

Entry	Catalyst (g)	Temp. (°C)	Solvent	Time (min.)	Yield (%)[b]
1	0.008	Reflux	EtOH	60	70
2	0.008	Reflux	CH_3CN	120	82
3	0.008	Reflux	n-Hexane	120	55
4	0.008	Reflux	CH_2Cl_2	120	34
5	0.008	Reflux	H_2O/EtOH(1:1)	20	90
6	0.008	Reflux	H_2O	10	98
7	0.008	100	Solvent-free	30	65
8	0.005	Reflux	H_2O	30	80
9	0.01	Reflux	H_2O	10	90
10	0.02	Reflux	H_2O	10	90
11	0.008	rt	H_2O	60	20
12	0.008	30	H_2O	60	60
13	0.008	50	H_2O	60	78
14	0.008	Reflux	H_2O	10	98
15	None	Reflux	EtOH	240	10
16	None	Reflux	H_2O	240	23

[a]Reaction conditions: 4-nitrobenzaldehyde (1 mmol), 4-hydroxycoumarin (2 mmol).
[b]Isolated yields.

Table 2. Fe_3O_4@ABM-EDTA catalyzed synthesis of biscoumarins in water.[a]



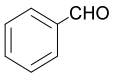
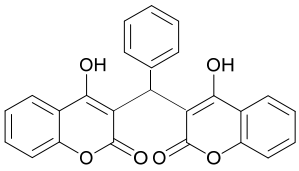
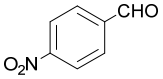
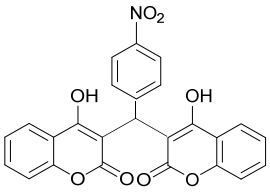
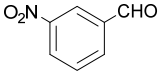
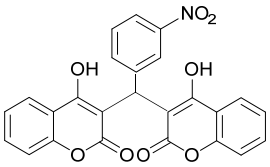
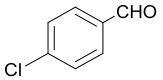
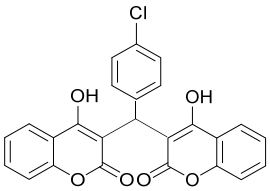
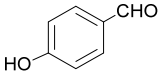
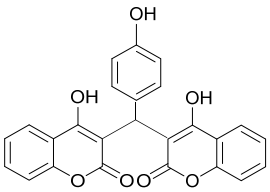
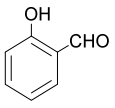
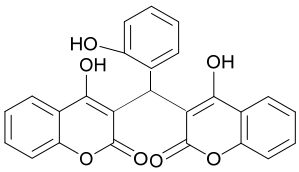
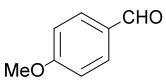
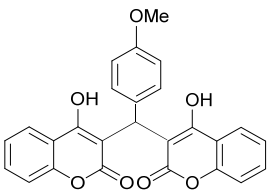
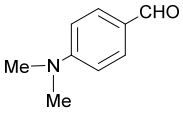
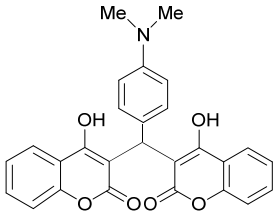
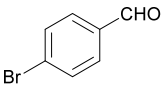
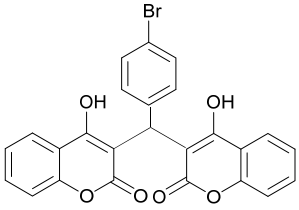
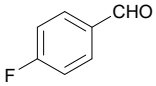
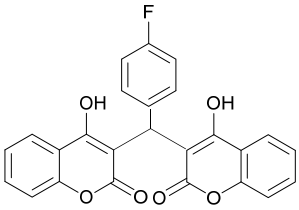
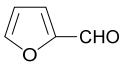
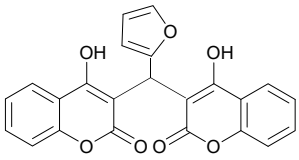
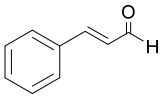
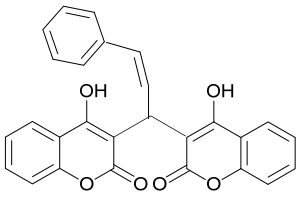
Entry	Aldehyde	Product	Time (min.)	Yield (%)[b]	m.p. (°C)		Ref.
					Found	Reported	
1			10	90	226-228	228-230	[20]
2			10	98	234-236	232-234	[20]
3			10	90	236-236	236-236	[22]
4			15	95	251-253	254-256	[20]
5			10	95	223-225	218-220	[20]
6			10	95	251-253	254-256	[22]
7			15	85	245-246	242-244	[20]

Table 2. (*Continued*).

8			10	90	221-222	222-224	[22]
9			10	92	264-265	266-268	[22]
10			10	85	212-213	212-214	[22]
11			10	90	194-196	198-200	[20]
12			10	95	225-227	228-230	[20]

[a]Reaction conditions: Aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol), Fe_3O_4@ABM-EDTA (0.008 g), water (3 ml), reflux.
[b]Isolated yields.

Table 3. Comparison results of Fe_3O_4@ABM-EDTA with some of other catalysts reported in the literature for the synthesis of biscoumarin derivatives.

Entry	Conditions	Catalyst	Time (min)	Yield (%)	Ref.
1	Water, 80 ℃	PTTH	7-10	80-95	[20]
2	Toluene, 90 ℃	[P4VPy–$BuSO_3H$]HSO_4	36-60	90-95	[21]
3	Ethanol, Reflux	$[TBA]_2[W_6O_{19}]$	5-10	85-92	[19]
4	CH_2Cl_2, 40 ℃	Nano silica chloride	1-5.5 h	68-95	[22]
5	H_2O, Reflux	SBPDSA	5-15	80-95	[23]
6	H_2O, Reflux	Fe_3O_4@ABM-EDTA	10-15	85-98	This work

4. Conclusions

In summary, we have prepared the Fe_3O_4@ABM-EDTA as an efficient and environmentally friendly catalyst that catalyzed the synthesis of biscoumarin derivatives in water. The procedures are clean, simple and safe. The catalyst was stable, magnetically recovered and recycled for several runs without any significant loss of efficiency. Moreover, heterogeneous reaction conditions, high yields of products, short reaction times, ease of work-up and clean procedure will make this procedure a useful addition to the available methods.

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